ANALYSIS OF WATERS AND INTERPRETATION OF THE RESULTS.

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PURPOSES OF THE ANALYSIS OF WATERS.

There are several kinds of analyses that may be made of samples of water, all very different in their scope and purpose. A sanitary analysis may be desired to determine the adaptability of water for drinking purposes. An analysis of water for irrigation may be desired, which would include the determination of various salts, harmful, helpful, or practically neutral in their effect on vegetation. A mineral analysis of water may be required to determine whether it contains compounds with marked medicinal qualities, or an analysis of water for boiler purposes may be desired that would include the determination of the substances in solution which would either form scales or injure the boiler by directly attacking the iron plates. There are other purposes for which water may be used and for which special determinations are often made, as, for example, in different manufacturing enterprises; but these are so varied and of so little interest to the general public that they will not be considered in this paper.

SANITARY WATER ANALYSIS.

In examining a water for sanitary purposes those constituents are quantitatively determined which show whether it has been contaminated with foreign matter, such as general sewage, human and animal excrement, etc. The determinations usually made are chlorin, free and albuminoid ammonia, nitrites, nitrates, oxygen-consuming capacity, and total solids.

CHLORIN.

Chlorin is present to some extent in nearly all waters, because it is dissolved from both the soil and air, usually as sodium chlorid. There is another source from which sodium chlorid (common salt) may be derived, that is, from sewage, and especially from the urine of human beings. This is, therefore, one of the most important constituents to be determined in a water analysis of this character. If the amount of chlorin is high, it is a general indication of contamination from human urine, but this is not always the case. In certain districts the

sodium chlorid in all waters is high, because the soil is rich in this constituent, or because a body of salt water is near by. The only way we can judge, therefore, whether this salt is naturally present or is introduced by sewage is to know the amount of sodium chlorid in waters of the same district which are of undoubted purity. If the amount of chlorin in the water under examination is markedly higher than this so-called "local normal," human contamination is strongly to be suspected.

FREE AND ALBUMINOID AMMONIA.

Free and albuminoid ammonia are present in small amounts in practically all waters, but when present in large amounts they usually indicate organic contamination, especially of animal origin, since organic matter from animal sources contains much more nitrogen than does vegetable organic matter. Free ammonia is not in itself injurious, but indicates that nitrogenous organic matter has been present, which, through the agency of oxygen, bacteria, etc., has been transformed into harmless ammonia. Of course, if organic matter has been present, the water may still contain chemical bodies, or bacteria which would have a very injurious effect upon the system. Albuminoid ammonia is not present already formed in the water, but is formed from nitrogenous organic bodies by treating them with an alkaline solution of potassium permanganate. A large amount of this substance usually indicates that organic matter, in a fresh or semiputrid condition, is present. Just as there are exceptions to most rules there are exceptions to the general rule that high figures for free and albuminoid ammonia indicate harmful organic contamination. For example, in many deep wells that are known to be pure, the free ammonia often runs as high as 0.70 to 0.80 part per million, while the amount that is ordinarily present in pure water is seldom above 0.05 to 0.10 part per million. This is doubtless due to the reduction of nitrates that have been formed in the soil in times past by sulphid of iron or some other harmless agent at the bottom of the well. Rain water, also, especially when gathered near large cities, contains quite a large amount of free ammonia that has been washed from the air. Again, albuminoid ammonia often runs rather high, say 0.20 to 0.40 part per million in streams which contain much living plant life, the water from which is not on that account objectionable.

NITRITES.

Nitrites in water are usually formed from ammonia by the action of nitrifying organisms upon this compound, and are the connecting link between ammonia on the one hand and the fully oxidized nitrates on the other. They may also be formed by the reducing action of a large amount of organic matter upon nitrates. Since nitrites are not

permanent and are only transition products, their presence, even in small amounts, usually indicates that active fermentation is going on and that the water is not able to fully oxidize the harmful organic matter into harmless nitrates. Whenever they occur in surface waters organic contamination is to be strongly suspected. In some cases nitrites may occur in waters without indicating contamination. Many springs and deep wells, for example, which can not in any way be contaminated, contain nitrites which are not present as a transition step in the oxidation of organic matter, but are formed from nitrates in the soil by the reduction of these bodies by ferrous iron and other reducing substances. The accepted standard for American rivers, as proposed by the late Professor Leeds, is 0.003 part of nitrogen as nitrite per million.

NITRATES.

Nitrates in water are the final oxidation product of the nitrogen of organic matter, and when present in at all large quantities indicate that nitrogenous organic matter (especially animal matter) has been present in the water and bas been oxidized. Because a large amount of the nitrogen of organic matter has been converted by oxidation into harmless nitrates it does not necessarily follow that the water is fit for use, since bacteria may remain which would give rise to disease. Nitrates are present in nearly all waters in small amounts, and the amount naturally present is much higher in some localities than in others. A "local normal," therefore, is of great aid in judging of the purity or nonpurity of any particular sample in so far as nitrates are concerned.

OXYGEN-CONSUMING CAPACITY.

The oxygen-consuming capacity figure in water analysis gives some idea of the amount of organic matter present, especially that of vegetable origin, since it is a rough measure of the amount of organic carbon contained in the water. A large figure does not necessarily indicate that the water is unfit for drinking purposes, as in many peaty streams the organic matter of vegetable origin may be very high and yet the water be unobjectionable. It is only when the oxygenconsuming capacity is judged, in conjunction with the other figures obtained, that any conclusion of a positive nature in regard to potability can be drawn. For example, if the albuminoid ammonia is high and the oxygen-consuming capacity also, the presence of organic matter of vegetable origin is indicated. If the albuminoid ammonia is high and the oxygen-consuming capacity is low, the presence of organic matter of animal origin is indicated. In the latter case, if the figure for chlorin is markedly above the "local normal," contamination from a privy is to be strongly suspected.

TOTAL SOLIDS.

While the determination of total solids in water is nearly always made, there is no figure in water analysis which shows so little its adaptability for drinking purposes as this one. If the figure is extremely high, salts which have a marked physiological action may be suspected, but they are not necessarily present. Some water analysts would cast aside all doubt as to the utility of this figure by declaring that waters containing above 686 parts per million are to be condemned, but such is not the case, as there are many instances, especially in the West, of water containing 1,200 parts per million and over being used without apparent evil results. It is, of course, self-evident that when the salts are high it depends more on what salts are present than on the amount of them whether or not the water is fit for drinking purposes.

In some cases other constituents of water are determined in a sanitary analysis, as the phosphates, which indicate whether urine has contaminated the water; determinations are also made of its odor, color, or taste, all of which information is sometimes useful, but seldom leads to definite conclusions.

CONCLUSIONS REGARDING ANALYSIS OF WATERS FOR SANITARY PURPOSES.

From what has been said above, concerning the various determinations to be made in a drinking water, it will be seen how misleading is the judgment of a sample of water from any one figure. All of the constituents and their amount must be taken into consideration when passing upon any particular sample. Since there are also exceptions to the general rules laid down above, a complete history of each sample of water is necessary to enable the analyst to judge whether certain of the figures are high, because of contamination, or by reason of some totally unobjectionable cause.

There are certain points that should be borne in mind when considering a sanitary analysis of water, viz, when all the figures are high or certain ones are extremely high, the chemist can usually say with a reasonable degree of certainty that the water is contaminated; but in some cases all of the figures may be low, thus indicating to the chemist that the water is perfectly healthful and yet bacteria may be present which would have a very injurious effect upon the health of the consumer. In such cases as the latter, a sanitary analysis serves only as an indication, and not as a proof, and should be accompanied by a bacteriological examination to give results of a positive nature.

ANALYSIS OF WATERS FOR IRRIGATION PURPOSES.

In making an analysis of a water for irrigation purposes the following determinations are usually made: Silica, carbonic acid, bicarbonic acid, sulphuric acid, chlorin, calcium, magnesium, sodium, potassium,

phosphoric acid, and nitric acid. The first eight constituents give some idea as to whether the water will or will not be harmful to vegetation. The last three represent the most important plant foods, and thus give an idea of the beneficial effects that may be expected from the use of water containing them. Suspended matter is also determined for reasons that will appear later.

The constituents, excluding silica, do not usually occur as the free acids or bases, but are combined to form salts. A number of the following are present, in larger or smaller quantities, in irrigation waters: Calcium carbonate or bicarbonate, magnesium carbonate or bicarbonate, potassium carbonate or bicarbonate, sodium carbonate or bicarbonate, calcium sulphate, magnesium sulphate, potassium sulphate, sodium sulphate, calcium chlorid, magnesium chlorid, potassium chlorid, sodium chlorid, sodium nitrate, and sodium phosphate.

CARBONATES.

Calcium carbonate or bicarbonate is present in practically all irrigation waters, to a greater or less extent, usually in the latter form, since calcium carbonate is quite insoluble. Neither one of these salts is considered as being especially significant in an irrigation water, since they are not injurious to vegetation. Calcium carbonate may be helpful both in modifying the physical state of a soil and in favoring nitrification. There seems to be only one case in which a large excess of calcium carbonate in water might be injurious, and that is when such a water is applied year after year to a land containing sodium sulphate. If such land is not well drained the calcium carbonate and sodium sulphate are apt to gather in the standing water and react upon one another, thus forming the highly injurious salt, sodium carbonate.

Magnesium carbonate or bicarbonate is also nearly always present in irrigation water, but neither is considered of especial importance, since neither is of itself markedly injurious nor markedly beneficial to vegetation.

Potassium carbonate or bicarbonate does not occur in extremely large quantities in irrigation waters; and in so far as these do occur they are beneficial, since they furnish one of the necessary plant foods which is often deficient.

Sodium carbonate is that constituent of an irrigation water which when present in the land gives rise to "black alkali," so called because of the black spots that are formed by the action of this salt upon the humus of the soil. Sodium carbonate is one of the worst salts that can occur in an irrigation water, since it exerts a corrosive action upon the roots of plants, especially the young and tender roots.

Sodium bicarbonate has recently been shown to be less injurious to

plant life than sodium carbonate, a but waters containing a large amount of it should not be used, as such waters when evaporated from the land would probably leave behind most of the sodium bicarbonate, not as such, but as sodium carbonate, which would then form "black alkali" and corrode the roots of plants in the usual way.

SULPHATES.

Calcium sulphate is one of those salts which acts as an indirect plant food, and is often very beneficial when applied to the land in alkali regions, since it reacts with the harmful salt, sodium carbonate, to form the less harmful salt, sodium sulphate. That this may not appear to be antagonistic to the statement made above, that "calcium carbonate and sodium sulphate are apt to gather in the standing water and react upon one another, thus forming the highly injurious salt, sodium carbonate," it should be mentioned that this reaction is very likely a reversible one. If such is the case, calcium sulphate and sodium carbonate would under certain conditions react to form calcium carbonate and sodium sulphate, while under other conditions the action would be reversed, resulting in the formation of calcium sulphate and sodium carbonate from calcium carbonate and sodium sulphate.

Magnesium sulphate, which, with sodium sulphate and sodium chlorid, forms white alkali, is much milder in its action upon plants than sodium carbonate, yet, when present in large amounts, it also is injurious to growth, if not prohibitive. Irrigation waters should not be applied which contain an excessive amount of this compound, since it would collect from year to year and cause serious damage.

Potassium sulphate practically never occurs in very large quantities in irrigation waters, but, in so far as it does, is of benefit, since it furnishes one of the essential plant foods.

Sodium sulphate is the predominating constituent of white alkali. This salt is generally considered to be more injurious than magnesium sulphate, but less injurious than sodium carbonate, and waters containing a moderate amount of this salt may be used indefinitely. Irrigation waters containing large amounts of salts are apt to cause a rise or accumulation of white alkali in a short time.

CHLORIDS.

CALCIUM AND MAGNESIUM CHLORIDS do not occur in the usual irrigation waters in large quantities, and therefore their effect upon vegetation has not been as thoroughly worked out as that of the salts previously mentioned. Generally speaking, however, these two salts are supposed to be less injurious than sodium carbonate and more injurious than magnesium and sodium sulphates.

^a Report No. 71, Division of Soils, U. S. Dept. Agr., "Some mutual relations between alkali soils and vegetation."

Potassium chlorid is not present in irrigation waters in large quantities, but, in so far as it is present, is of benefit as a plant food.

Sodium chlorid, in considerable amounts, is almost as much to be feared in an irrigation water as is sodium carbonate. While it is not as corrosive as the latter compound it is harder to get rid of, since it can not be neutralized in the soil in any way, but must be removed by drainage. The more corrosive sodium carbonate may be neutralized to a great extent by treating the land with gypsum.

SODIUM NITRATE AND PHOSPHATE AND SUSPENDED MATTER.

Sodium nitrate and phosphate are present to a greater or less extent in most waters and are beneficial, since they supply those two essential plant foods, nitrogen and phosphoric acid.

Suspended matter.—A determination of the suspended matter in irrigation water is of value for two reasons. First, the suspended matter contains very appreciable amounts of the three principal plant foods—potash, phosphoric acid, and nitrogen. In the second place, the suspended matter or silt is a very important consideration in many rivers where the reservoirs and canals that hold the water soon fill up on account of the suspended matter settling out. Thus, we see that, while the suspended matter in irrigation waters is of value for one purpose, its presence in large amounts is much to be deplored from an economic standpoint.

ORDER IN WHICH INJURIOUS SALTS AFFECT VEGETATION.

All that has been said above concerning the various salts and their action upon plants refers to them as they usually occur in alkali regions, mixed with one another, and not to the action of the pure salts. The order, therefore, in which the various injurious salts affect vegetation, as determined by practical experience in alkali regions, and beginning with the most injurious, is approximately as follows: (1) Sodium carbonate; (2) sodium chlorid; (3) magnesium and calcium chlorid; (4) sodium sulphate; (5) magnesium sulphate.

Sodium bicarbonate is not entered in the above list, since, as far as the writer can discover, its action has not been noted in practical experiments.

Very recently Kearney and Cameron^a made a study of the effect of solutions of the pure salts found in irrigation waters and also of mixtures of these salts upon the roots of the white lupine and alfalfa. In pure solutions a determination was first made of the maximum concentration of salt that permitted a survival of the roots, and it was found that the salts acted in the following order, beginning with the most toxic: (1) Magnesium sulphate; (2) magnesium chlorid; (3) sodium

a Report No. 71, Division of Soils, U. S. Dept. Agr., "Some mutual relations between alkali soils and vegetation."

carbonate; (4) sodium sulphate; (5) sodium chlorid; (6) sodium bicarbonate; (7) calcium chlorid.

Further investigation showed that when each of these salts was mixed with any other of the salts the limit of endurance was nearly always changed to a marked extent. This was especially true when various salts were mixed with the nontoxic salts, calcium carbonate and calcium sulphate, in which case the limit of endurance was always raised very markedly. To a less extent this was also true for magnesium carbonate.

Each of the toxic salts was mixed with an excess of both calcium sulphate and calcium carbonate, and it was found that the limit of endurance of the roots was greatly increased, the order of toxicity being as follows, beginning with the most toxic: (1) Sodium carbonate; (2) sodium bicarbonate; (3) magnesium chlorid; (4) sodium chlorid; (5) calcium chlorid; (6) sodium sulphate; (7) magnesium sulphate.

Thus we see that when the various injurious salts are mixed with an excess of calcium sulphate and calcium carbonate, sodium carbonate is the most toxic and magnesium sulphate the least so. This order corresponds very closely to the order as given above, which has been found to be approximately correct in practical field experiments. This is what might be expected, since many of the alkali regions contain either calcium sulphate, calcium carbonate, or both, as well as the injurious salts.

It appears, therefore, that calcium carbonate and calcium sulphate especially, and magnesium carbonate to a less degree, when present in irrigation waters, must be regarded as extremely significant, since they have a marked mitigating effect on the toxic salts present in the soil. This has previously been recognized in the case of calcium sulphate when applied to lands containing sodium carbonate, but has not been generally recognized in the other instances.

AMOUNT OF SALTS ALLOWABLE IN IRRIGATION WATER.

The total quantity of salts allowable in an irrigation water and the quantity of each salt allowable, are hard problems to solve, since the answer depends upon so many conditions. One will at once note that since the various salts have a mitigating or nonmitigating effect upon one another, this must be taken into consideration in judging of water for irrigation purposes. For example, the same piece of land could stand much more of a water containing large amounts of both sodium sulphate and calcium sulphate in solution than it could stand of a water containing the same amount of sodium sulphate and but little calcium sulphate. Again, this would be true in the case of waters containing sodium chlorid and calcium sulphate, etc.

Further than this, the character of the land to be irrigated is perhaps the most important factor in judging of the irrigation water to be applied. On a heavy clay land, for example, which allows the water to percolate through very slowly, a water very free from toxic salts must be used, since not only would all the salts present in the water be retained in the soil, but the salts already present could not be washed out, even by heavy irrigation and drainage. Furthermore, if the water stands upon the land too long it is apt to cause swamping and so injure the physical condition of the soil. On the other hand, if water containing a large amount of injurious salts was applied to a very light sandy soil, a large quantity of the salts in the upper 4 or 5 feet could be washed down and drained off, and the salts that were contained in the water alone would not be enough to injure crops.

In regard to this question of the total amount of salts allowable in an irrigation water, Hilgard ^a says:

Broadly speaking, the extreme limit of mineral content usually assigned for potable waters, viz, 40 grains per gallon (686 parts per million), also applies to irrigation waters; yet it sometimes happens that all or most of the solid contents is gypsum and epsom salt, when only a large excess of the latter would constitute a bar to irrigation use. When, on the contrary, a large portion of the solids consists of carbonate of soda or common salt, even a smaller portion of salts than 40 grains per gallon might preclude its regular use, depending on the nature of the soil to be irrigated.

In certain portions of the country water containing much more than 40 grains per gallon of total solids can be applied with impunity. For example, in New Mexico, where sodium carbonate is seldom present and the soluble salts consist principally of sodium, magnesium, and calcium sulphates, water containing 1,000 parts per million total solids has been used upon trees for from eight to ten years without injury thereto. In the same Territory water containing 3,000 parts per million of total solids is used, but farmers are having trouble with alkali.

ANALYSIS OF MINERAL WATERS.

In making an analysis of mineral waters, all of the metal and acids held in solution should be determined, even though some are present in very small quantities, since it is upon very small amounts of certain substances that the distinctive character and physiological action of so many waters depend. The following substances are present in practically all waters, and are apt to be found in mineral waters in large quantities: Sodium, potassium, magnesium, calcium, iron, aluminum, chlorin, nitric acid, sulphuric acid, silica, carbonic acid, and bicarbonic acid.

The following constituents often appear in mineral waters, but usually in small quantities: Ammonia, lithium, manganese, barium, strontium, arsenic, iodin, bromin, fluorin, boric acid, phosphoric acid, nitrous acid, hydrogen sulphid, and a few other very rare elements.

In reporting these acids and bases they are joined to each other as salts, that is, to form chlorids, sulphates, carbonates, etc., of the various metals.

a Bulletin No. 140 of the California Agricultural Experiment Station.

^b Bulletin No. 34 of the New Mexico Agricultural Experiment Station.

CLASSIFICATION OF MINERAL WATERS.

The most scientific classification of mineral waters is that proposed by Dr. Albert C. Peale, and modified by Dr. J. K. Crook, as follows:

Scheme of classification of mineral waters.

Group A: Nonthermal.

Group B: Thermal.

Class I: Alkaline....Sulphated.

Muriated.

Class II: Alkaline Saline....Sulphated.

Muriated.

Class III: SalineSulphated.

Muriated.

Class IV: ChalybeateAlkaline.

Sulphated.

Class V: Neutral.

DISCUSSION OF THE CLASSES OF MINERAL WATERS.

The presence or absence of gas is expressed by the following terms: (1) Nongaseous; (2) carbonated, if carbon dioxid is present; (3) sulphuretted, if hydrogen sulphid is present, etc.

Class I includes those waters which contain the carbonates or bicarbonates of the alkali metals or the alkaline earths, as a predominating constituent. Such waters are used in the treatment of dyspepsia, especially acid dyspepsia. They act as a diuretic, correct acidity of the urine, etc.

Class II includes those waters which contain the carbonates and bicarbonates and sulphates or chlorids of the alkali or alkaline earth metals on approximately equal terms. Waters of this class have somewhat the same medicinal qualities as those of Class I and Class III.

Class III is made up of waters containing sulphates and chlorids in largely predominating amounts. The sulphated salines usually act as purgatives or laxatives, according to the amount used. They increase the activity of the liver, regulate the bowels, increase the flow of urine, etc.

The muriated salines generally contain sodium chlorid in large amounts. Waters containing common salt promote the flow of urine. They are of value in cases of indigestion, since they increase the flow of digestive fluids and prevent putrefactive changes in the intestines. The waters containing chlorids of calcium and magnesium are used principally as tonics.

Class IV includes those waters which contain iron as one of the principal and most active constituents. Such waters act directly as tonics, and are principally used in cases of anæmia and general debility.

Class V is composed of waters which contain only a small amount of mineral matter in solution. Although such waters do not contain enough of any particular salt to allow them to be classified under the four heads mentioned above, they may contain salts which have a very marked physiological action.

If waters were only classified as above, oftentimes very important constituents that are present in small amounts, but which are very active, would not be brought out sufficiently in the name. Therefore, in designating such waters the names of such active substances contained in small quantities are joined to the regular class name. For example, waters which contain sulphates in predominating amounts and a small amount of lithium would be termed sulphated saline-lithic waters. Those containing alkaline carbonates and alkaline chlorids in approximately equal quantities and a small amount of bromin would be called alkaline-muriated-saline-bromic waters, etc.

ANALYSIS OF WATER FOR BOILER PURPOSES.

In examining a water for boiler purposes the determination of the ingredients which form a scale or sludge, or act directly upon the iron plates of the boiler, is most important. Waters to be used for boilers are divided into three classes—hard, soft, and saline.

HARD WATERS.

Hard waters contain some or all of the following constituents: Calcium carbonate, magnesium carbonate, and calcium sulphate. first two of these constituents are held in solution by the presence of carbon dioxid, so that when such waters are boiled and the carbon dioxid is driven off, calcium and magnesium carbonates are precipitated. Therefore, hardness due to these salts can be removed by boiling, and is termed "temporary hardness." When the hardness is due to calcium sulphate, which is not removed by boiling, it is termed "permanent hardness." If the hardness of a water is only temporary it can often be used with fair results, since the two carbonates causing this kind of hardness do not usually form a hard scale, but rather a sludge that can be blown off. In case the temporary hardness is so extreme that the removal of the calcium and magnesium carbonates is necessary, this can easily be effected by treating the water with limewater or sodium hydrate, either of which joins with the carbon dioxid present in the water, and thus precipitates the carbonates.

Waters, however, that contain calcium sulphate or calcium sulphate and calcium and magnesium carbonates form a hard scale which must be chipped off. This hard scale is due to the presence of calcium sulphate, which is precipitated at the high temperature attained by the water under steam pressure. The evil effects resulting from permanent hardness can be mitigated by treating the water with sodium

carbonate, which forms the less harmful compound, calcium carbonate. It is evident that a scale formed around the boiler will result in the loss of a large amount of heat. It has been found by experience that a one-fourth inch incrustation or scale causes a waste of about 50 per cent of the heat applied.

SOFT WATERS.

Soft waters are those which do not contain a large amount of mineral matter in solution. The only ingredient in waters of this class that is apt to cause trouble is organic matter that may be dissolved as organic acids and corrode the boiler plates.

SALINE WATERS.

Saline waters are those which contain a large amount of salts in solution, but not the incrusting salts. Such waters as these are well exemplified by many of the Western streams and by sea water. When waters containing a very large amount of soluble salts, as the saline waters, are used in a boiler, a point is finally reached when the water deposits its soluble salts. When this point is reached the boiler should be blown off.

There is one ingredient that may occur in any of the above waters, but which most often occurs in the saline waters, that is worthy of attention. This is magnesium chlorid, which, under the great heat that exists in boilers, is acted upon by the water, and magnesium hydroxid and hydrochloric acid are formed. Of course, the hydrochloric acid attacks the boiler plates, while the magnesium hydroxid helps to form a scale.

DETERMINATIONS NECESSARY IN BOILER WATERS.

In making an analysis of a boiler water, therefore, the following determinations are necessary: Carbonic and bicarbonic acids, free acids other than carbonic and bicarbonic acids, chlorin, sulphuric acid, calcium, and magnesium. In order that these bases and acids may be combined as salts according to the usually accepted method, determinations of iron, aluminum, sodium, potassium, and occasionally nitric acid are also necessary. The determination of silica is often included, and sometimes in peaty waters the determination of organic matter.

It is thus evident that in making a water analysis the substances to be determined and the interpretation of the results depend entirely upon the purpose for which the analysis is desired, and that in nearly all cases a history of the water is extremely helpful, while in some cases it is absolutely necessary.